**Palladium(II)-Catalyzed Oxidative Transformation of Allylic Alcohols and Vinyl Ethers
into 2-Alkoxytetrahydrofurans: Catechol as an Activator of Catalyst**

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Supporting Information

General: NMR spectra were recorded on a Varian ^{UNITY} INOVA 400 (¹H NMR, 399.91 MHz ; ¹³C NMR, 100.56 MHz) instrument for solutions in CDCl₃ with Me₄Si as an internal standard. Infrared spectra were measured on a JASCO FTIR-610 spectrometer. Elemental analyses were performed on Elementary VarioEL *III*. GLC analyses were performed on a Shimadzu GC-17A instrument by using DB-1 glass capillary column (0.53 mm x 30 m) under the conditions of injection temperature (200 °C), column temperature (60 - 250 °C), and nitrogen gas pressure (0.5 kg/ cm²) with flame-ionization detectors and nitrogen as carrier gas. GC yields were determined using tetraethylene glycol dimethyl ether or anisole as an internal standard. Mass spectrum was obtained on a Shimadzu GCMS-QP5050 gas chromatograph-mass spectrometer at 0.7 eV by using DB-1 glass capillary column (0.25 mm x 30 m) under the conditions of injection temperature (200 °C), column temperature (60 - 250 °C), and helium gas pressure (0.5 kg/ cm²). All melting points were measured on Yanaco micro melting point apparatus and were uncorrected. Analytical thin layer chromatography (TLC) was performed with Merck silica gel 60 F₂₅₄ plates. Column chromatography was performed with Merck silica gel 60.

Materials: Allyl alcohol, (*E*)-3-phenyl-2-propen-1-ol (cinnamyl alcohol), tetraethylene glycol dimethyl ether, and copper(II) acetate were commercially available from Wako Pure Chemical Industries, Ltd. *n*-Butyl vinyl ether, ethyl vinyl ether, catechol, and palladium(II) acetate were commercially available from Nakarai Tesque, Inc. (*E*)-3-(4-Nitrophenyl)-2-propen-1-ol (4-nitrocinnamyl alcohol) was obtained from Aldrich. 2-Buten-1-ol (crotyl alcohol) and 2-vinyloxytetrahydropyran were commercially available from TOKYO KASEI KOGYO, Co. Ltd.

Synthesis of (*Z*)-4-Benzylidene-2-ethoxytetrahydrofuran (**3a**).

Pd(OAc)₂ (11.2 mg, 0.05 mmol), Cu(OAc)₂ (9.1 mg, 0.05 mmol), and catechol (11.0 mg, 0.1 mmol) were dissolved in MeCN (0.5 mL) in a 25 mL side-armed round bottomed flask under O₂ (balloon), and the mixture was stirred for 30 min at room temperature. Ethyl vinyl ether (288 mg, 4.0 mmol) was added to the flask, and a solution of (*E*)-3-phenyl-2-propen-1-ol (134 mg, 1.0 mmol) in MeCN (0.5 mL) was then added. After the reaction mixture was stirred for 3 h at room temperature, GC yield of **3a** was determined to be 84% by using tetraethylene glycol dimethyl ether as an internal standard. Isolation of pure **3a** was made as follows. The same reaction as above was separately performed, and the reaction mixture was stirred for 3h. After filtration through Florisil column (10 mm x 80 mm 3 g, EtOAc / *n*-hexane = 1 / 20), the solvent was evaporated under reduced pressure. The product **3a** nearly pure was obtained in 82% yield (168 mg, 0.82 mmol), and further purification was made by thin-layer chromatography on silica gel.

3a :

Rf : 0.62 (EtOAc / *n*-hexane = 1 / 20).

bp (bulb-to-bulb) : 145 - 146 °C (1 mmHg).

¹H NMR (400 MHz, CDCl₃) δ 1.21 (t, J= 7.1 Hz, 3H), 2.72 (d, J= 16.2 Hz, 1H), 2.94 (dd, J= 16.2, 5.1 Hz, 1H), 3.50 (dq, J= 9.3, 7.1 Hz, 1H), 3.77 (dq, J= 9.3, 7.1 Hz, 1H), 4.68 (d, J= 2.1 Hz, 1H), 4.69 (d, J= 2.1 Hz, 1H), 5.23 (d, J= 5.1 Hz, 1H), 6.42 (s, 1H), 7.12 (d, J= 7.2 Hz, 2H), 7.19 (t, J= 7.2 Hz, 1H), 7.33 (t, J= 7.2 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 15.14, 41.12, 62.57, 67.85, 101.93, 121.55, 126.40, 127.78, 128.39, 137.34, 138.98.

FTIR (neat, cm⁻¹) : 3053, 3025, 1739, 1598, 1184, 1095, 1032, 997.

GCMS m/e 204 (M⁺).

Anal. Calcd for C₁₃H₁₆O₂: C, 76.42; H, 7.89. Found: C, 76.32; H, 7.49.

Synthesis of (*Z*)-4-Benzylidene-2-*n*-buthoxytetrahydrofuran (3b**).**

Pd(OAc)₂ (11.2 mg, 0.05 mmol), Cu(OAc)₂ (9.1 mg, 0.05 mmol), and catechol (11.0 mg, 0.05 mmol) were dissolved in MeCN (0.5 mL) in a 25 mL side-armed round bottomed flask under O₂ (balloon), and the mixture was stirred for 30 min at room temperature. *n*-Buthyl vinyl ether (401 mg, 4.0 mmol) was added to the flask, and a solution of (*E*)-3-phenyl-2-propen-1-ol (134 mg, 1.0 mmol) in MeCN (0.5 mL) was then added. After the reaction mixture was stirred for 3 h at room temperature, the mixture was filtered through Florisil column (10 mm x 80 mm 3 g, *n*-hexane), and the solvent was evaporated under reduced pressure to give the product **3b** (173 mg, 0.74 mmol, 74%) in nearly pure form. Further purification was made by thin-layer chromatography on silica gel.

3b :

Rf : 0.67 (EtOAc / *n*-hexane = 1 / 9).

bp (bulb-to-bulb) : 173 - 175 °C (5 mmHg).

¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, J= 7.5 Hz, 3H), 1.36 (tq, J= 8.4, 7.5 Hz, 2H), 1.56 (tt, J= 8.4, 6.6 Hz, 2H), 2.71 (d, J= 16.4, 1H), 2.93 (dd, J= 16.4, 5.1 Hz, 1H), 3.44 (dt, J= 9.5, 6.6 Hz, 1H), 3.71 (dt, J= 9.5, 6.6 Hz, 1H), 4.68 (d, J= 2.3 Hz, 1H), 4.69 (d, J= 2.3 Hz, 1H), 5.21 (d, J= 5.1 Hz, 1H), 6.42 (s, 1H), 7.13 (d, J= 7.3 Hz, 2H), 7.20 (t, J= 7.3 Hz, 1H), 7.34 (t, J= 7.3 Hz, 2 H).

¹³C NMR (101 MHz, CDCl₃) δ 13.86, 19.34, 31.70, 41.09, 67.04, 67.87, 102.15, 121.51, 126.42, 127.81, 128.44, 137.40, 139.12.

FTIR (neat, cm⁻¹) : 3026, 2930, 2870, 1599, 1492, 1449, 1423, 1345, 1180, 1097, 1038, 925, 840, 749, 695.

GCMS m/e 232 (M⁺).

Anal. Calcd for C₁₅H₂₀O₂: C, 77.55; H, 8.68. Found: C, 77.53; H, 8.62.

Synthesis of 2-Ethoxy-(*Z*)-4-(4-nitrobenzylidene)tetrahydrofuran (3c).

Pd(OAc)₂ (11.2 mg, 0.05 mmol), Cu(OAc)₂ (9.1 mg, 0.05 mmol), and catechol (11.0 mg, 0.1 mmol) were dissolved in MeCN (1.0 mL) in a 25 mL side-armed round bottomed flask under O₂ (balloon), and the mixture was stirred for 30 min at room temperature. Ethyl vinyl ether (288 mg, 4.0 mmol) was added to the flask, and (*E*)-3-(4-nitrophenyl)-2-propen-1-ol (179 mg, 1.0 mmol) was then added. After the reaction mixture was stirred for 12 h at room temperature, the mixture was filtered through Florisil column (10 mm x 130 mm 4 g, EtOAc), and the solvent was evaporated under reduced pressure to gave **3c** (241 mg, 0.96 mmol, 96% yield) in solid state. Purification was made by recrystallization from hexane and EtOAc (5 : 1).

3c :

mp : 75 - 76 °C.

¹H NMR (400 MHz, CDCl₃) δ 1.21 (t, J= 7.1 Hz, 3H), 2.80 (d, J= 16.9 Hz, 1H), 2.98 (dd, J= 16.9, 4.9 Hz, 1H), 3.52 (dq, J= 8.5, 7.1 Hz, 1H), 3.78 (dq, J= 8.5, 7.1 Hz, 1H), 4.71 (d, J= 2.4 Hz, 1H), 4.72 (d, J= 2.4 Hz, 1H), 5.27 (d, J= 4.9 Hz, 1H), 6.51 (s, 1H), 7.20 (d, J= 8.9 Hz, 2H), 8.20 (d, J= 8.9 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 15.13, 41.64, 62.81, 67.81, 101.87, 120.01, 123.88, 128.24, 143.67, 144.96, 145.93.

FTIR (nujol, cm⁻¹) : 2927, 1652, 1592, 1513, 1099, 1049, 996.

GCMS m/e 249 (M⁺).

Anal. Calcd for C₁₃H₁₅NO₄: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.64; H, 6.07; N, 5.50.

Synthesis of (*Z*)-4-Benzyliden-2-tetrahydropyranyloxytetrahydrofuran (**3d**).

Pd(OAc)₂ (22.5 mg, 0.1 mmol), Cu(OAc)₂ (18.2 mg, 0.1 mmol), and catechol (22.0 mg, 0.2 mmol) were dissolved in MeCN (0.5 mL) in a 25 mL side-armed round bottomed flask under O₂ (balloon), and the mixture was stirred for 30 min at room temperature. 2-Vinyloxytetrahydropyran (513 mg, 4.0 mmol) was added to the flask, and a solution of (*E*)-3-phenyl-2-propen-1-ol (134 mg, 1.0 mmol) in MeCN (0.5 mL) was then added. After the reaction mixture was stirred for 6 h at room temperature, the mixture was filtered through Florisil column (10 mm x 80 mm 3 g, EtOAc / *n*-hexane = 1 / 20), and the solvent was evaporated under reduced pressure to give a mixture of *R*^{*}*R*^{*}- and *R*^{*}*S*^{*}-**3d**. Isolation of each isomer by thin-layer chromatography gave *R*^{*}*R*^{*}-**3d** (164 mg, 0.63 mmol) and *R*^{*}*S*^{*}-**3d** (24 mg, 0.09 mmol). The product yield of **3d** thus corresponds to 72% (*R*^{*}*R*^{*}/*R*^{*}*S*^{*} = 87/13). The configuration of *R*^{*}*R*^{*} and *R*^{*}*S*^{*} was assigned on the bases of X-ray analysis of the corresponding *R*^{*}*R*^{*}-**3e** (see page S11).

R^{*}*R*^{*}-**3d** :

Rf : 0.5 (EtOAc / *n*-hexane = 1 / 4)

bp (bulb-to-bulb) : 176 - 178 °C (4 mmHg).

¹H NMR (400 MHz, CDCl₃) δ 1.47-1.61 (m, 4H), 1.66-1.74 (m, 1H), 1.76-1.86 (m, 1H), 2.77 (d, J= 16.6, 1H), 2.98 (dd, J= 16.6, 4.96 Hz, 1H), 3.51-3.57 (m, 1H), 3.85-3.92 (m, 1H), 4.68 (d, J= 14.4 Hz, 1H), 4.70 (d, J= 14.4 Hz, 1H), 4.95 (s, 1H), 5.27 (d, J= 5.6 Hz, 1H), 6.44 (s, 1H), 7.13 (d, J= 7.8 Hz, 2H), 7.20 (t, J= 7.8 Hz, 1H), 7.33 (t, J= 7.8 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 19.90, 25.36, 30.66, 40.76, 63.25, 68.07, 94.78, 97.86, 121.62, 126.45, 127.77, 128.44, 137.34, 138.88.

FTIR (neat, cm⁻¹) : 3036, 2942, 2858, 1718, 1713, 1492, 1449, 1350, 1272, 1201, 1118, 1074.

GCMS m/e 260 (M⁺).

R^{*}*S*^{*}-**3d** :

Rf : 0.4 (EtOAc / *n*-hexane = 1 / 4).

bp (bulb-to-bulb) : 132 - 135 °C (1 mmHg).

¹H NMR (400MHz, CDCl₃) δ 1.46-1.66 (m, 4H), 1.67-1.76 (m, 1H), 1.76-1.85 (m, 1H), 2.77 (d, J= 16.3, 1H), 2.97 (dd, J= 16.3, 4.56 Hz, 1H), 3.52-3.59 (m, 1H), 3.94-4.01 (m, 1H), 4.71 (d, J= 14.2 Hz, 1H), 4.83 (d, J= 14.2 Hz, 1H), 4.85 (s, 1H), 5.45 (d, J= 5.4 Hz, 1H), 6.42 (s, 1H), 7.13 (d, J= 7.7 Hz, 2H), 7.20 (t, J= 7.7 Hz, 1H), 7.33 (t, J= 7.7 Hz, 2H).

Synthesis of (*Z*)-4-(4-Nitrobenzyliden)-2-tetrahydropyranyloxytetrahydrofuran (3e**).**

Pd(OAc)₂ (11.2 mg, 0.05 mmol), Cu(OAc)₂ (9.1 mg, 0.05 mmol), and catechol (11.0 mg, 0.1 mmol) were dissolved in MeCN (1.0 mL) in a 25 mL side-armed round bottomed flask under O₂ (balloon), and the mixture was stirred for 30 min at room temperature. 2-Vinyloxytetrahydropyran (513 mg, 4.0 mmol) was added to the flask, and (*E*)-3-(4-nitrophenyl)-2-propen-1-ol (179 mg, 1.0 mmol) was then added. After the reaction mixture was stirred for the 24 h at room temperature, the mixture was filtered through Florisil column (10 mm x 60 mm 2.5 g, EtOAc / *n*-hexane = 1 / 20), and the solvent was evaporated under reduced pressure to give a mixture of *R*^{*}*R*^{*}- and *R*^{*}*S*^{*}-**3e**. Isolation of each isomer by thin-layer chromatography gave *R*^{*}*R*^{*}-**3e** (205 mg, 0.67 mmol) in solid state and *R*^{*}*S*^{*}-**3e** (35 mg, 0.11 mmol) as liquid. The product yield of **3e** thus corresponds to 78% (*R*^{*}*R*^{*}/*R*^{*}*S*^{*} = 86/14). Purification was made by recrystallization from hexane and diethyl ether (3 : 1). The configuration of *R*^{*}*R*^{*} and *R*^{*}*S*^{*} was assigned on the basis of X-ray analysis of *R*^{*}*R*^{*}-**3e** (see page S11).

***R*^{*}*R*^{*}-**3e** :**

Rf : 0.35 (EtOAc / *n*-hexane = 1 / 4).

mp : 92 - 93 °C.

¹H NMR (400 MHz, CDCl₃) δ 1.47-1.63 (m, 4H), 1.68-1.77 (m, 1H), 1.79-1.87 (m, 1H), 2.83 (d, J= 16.8, 1H), 3.03 (dd, J= 16.8, 4.9 Hz, 1H), 3.52-3.59 (m, 1H), 3.86-3.92 (m, 1H), 4.59 (d, 12.8 Hz, 1H), 4.63 (d, 12.8 Hz, 1H), 4.95 (s, 1H), 5.65 (d, J= 4.9 Hz, 1H), 6.53 (s, 1H), 7.26 (d, J= 8.76 Hz, 2H), 8.21 (d, J= 8.76 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 19.83, 25.31, 30.59, 41.23, 63.26, 68.00, 94.82, 97.74, 120.07, 123.87, 128.21, 143.62 144.83, 145.88.

FTIR (KBr, cm⁻¹) : 3078, 2955, 2929, 1657, 1593, 1340, 1119, 989, 973, 924, 749, 688.

GCMS m/e 305 (M⁺).

Anal. Calcd for C₁₆H₁₉NO₅: C, 62.94; H, 6.27; N, 4.59. Found: C, 62.87; H, 6.57; N, 4.49.

R^{*}S^{*}-3e :

Rf : 0.24 (EtOAc / *n*-hexane = 1 / 4).

¹H NMR (400 MHz, CDCl₃) δ 1.48-1.64 (m, 4H), 1.67-1.78 (m, 1H), 1.78-1.86 (m, 1H), 2.83 (d, J= 16.6 Hz 1H,), 3.03 (dd, J= 16.6, 4.5 Hz, 1H), 3.52-3.63 (m, 1H), 3.95-4.06 (m, 1H), 4.75 (d, J= 14.3 Hz, 1H), 4.88 (d, J= 14.3 Hz, 1H), 4.91(s, 1H), 5.50 (d, J= 4.5 Hz, 1H), 6.53 (s, 1H), 7.45 (d, J= 8.9 Hz, 2H), 8.20 (d, J= 8.9 Hz, 2H).

Synthesis of 2-*n*-Butoxy-4-methylenetetrahydrofuran (3f).

Pd(OAc)₂ (11.2 mg, 0.05 mmol), Cu(OAc)₂ (9.1 mg, 0.05 mmol), and catechol (11.0 mg, 0.1 mmol) were dissolved in MeCN (0.5 mL) in a 25 mL side-armed round bottomed flask under O₂ (balloon), and the mixture was stirred for 30 min at room temperature. *n*-Butyl vinyl ether (401 mg, 4.0 mmol) was added to the flask, and a solution of allyl alcohol (58 mg, 1.0 mmol) in MeCN (0.5 mL) was then added. After the reaction mixture was stirred for 3 h at room temperature, GC yield of **3f** was determined to be 74% by using tetraethylene glycol dimethyl ether as an internal standard. The reaction mixture was filtered through Florisil column (17 mm x 80 mm 6g, *n*-hexane), and the solvent was evaporated under reduced pressure to give **3f** (115 mg, 0.73 mmol, 73% yield) in nearly pure form.

3f :

bp (bulb-to-bulb) : 54 - 55 °C (4 mmHg).

¹H NMR (400 MHz, CDCl₃) δ 0.83 (t, J= 7.5 Hz, 3H), 1.29 (tq, J= 8.4, 7.5 Hz, 2H), 1.47 (tt, J= 8.4, 6.6 Hz, 2H), 2.43 (d, J= 16.3 Hz, 1H), 2.61 (dd, J= 16.3, 5.2 Hz, 1H), 3.33 (dt, J= 9.3, 7.5 Hz, 1H), 3.61 (dt, J= 9.3, 7.5 Hz, 1H), 4.26 (d, J= 12.4 Hz, 1H), 4.31 (d, J= 12.4 Hz, 1H), 4.98 (s, 1H), 5.03 (s, 1H), 5.11 (d, J= 5.2 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 13.65, 19.18, 31.55, 39.16, 66.75, 68.90, 103.50, 104.55,

145.64.

FTIR (neat, cm^{-1}) : 3081, 2960, 2871, 1714, 1671, 921, 883, 735.

GCMS m/e 156 (M^+).

Synthesis of 2-*n*-Butoxy-4-vinyltetrahydrofuran (**3g**).

$\text{Pd}(\text{OAc})_2$ (11.2 mg, 0.05 mmol), $\text{Cu}(\text{OAc})_2$ (9.1 mg, 0.05 mmol), and catechol (11.0 mg, 0.1 mmol) were dissolved in MeCN (0.5 mL) in a 25 mL side-armed round bottomed flask under O_2 (balloon), and the mixture was stirred for 30 min at room temperature. *n*-Buthyl vinyl ether (401 mg, 4.0 mmol) was added to the flask, and a solution of 2-buten-1-ol (*trans/cis* = 5/1, 72 mg, 1.0 mmol) in MeCN (0.5 mL) was then added. After the reaction mixture was stirred for 3 h at room temperature, GC yield of **3g** was determined to be 74% by using anisole as an internal standard. The reaction mixture was filtered through Florisil column (11 mm x 80 mm 2.8 g, EtOAc, 100 mL), and the solvent was evaporated under reduced pressure to give a 71:29 mixture of *trans*- and *cis*-**3g**. The ratio was determined by NMR. Purification was made by bulb-to-bulb distillation.

3g :

bp (bulb-to-bulb) : 102 - 105 °C (4 mmHg).

^1H NMR (400 MHz, CDCl_3) δ 0.87 (t, J = 7.3 Hz, 0.9H, [*trans*]), 0.88 (t, J = 7.3 Hz, 2.1H, [*cis*]), 1.33 (sex, J = 7.3 Hz, 0.6H, [*trans*]), 1.33 (sex, J = 7.3 Hz, 1.4H, [*cis*]), 1.61 (ddd, J = 13.4, 8.8, 2.9 Hz, 0.7H, [*cis*]), 1.70 (ddd, J = 14.4, 8.5, 5.2 Hz, 0.3H, [*trans*]), 2.02 (ddd, J = 14.4, 8.5 Hz, 0.3H, [*trans*]), 2.32 (ddd, J = 13.4, 8.8, 5.9 Hz, 0.7H, [*cis*]), 2.75 (sex, J = 8.5 Hz, 0.7H, [*cis*]), 3.02 (sex, J = 8.3 Hz, 0.3H, [*trans*]), 3.28 (dt, J = 9.6, 7.3 Hz, 0.3H, [*trans*]), 3.30 (dt, J = 9.5, 7.3 Hz, 0.7H, [*cis*]), 3.55 (dd, J = 8.8, 8.8 Hz, 0.7 H, [*cis*]), 3.55 (dd, J = 8.5, 8.5 Hz, 0.3H, [*trans*]), 3.65 (dt, J = 9.6, 7.3 Hz, 0.3H, [*trans*]), 3.66 (dt, J = 9.5, 7.3 Hz, 0.7H, [*cis*]), 3.92 (m, 1H), 3.92 (dd, J = 8.8, 8.8 Hz, 0.7H, [*cis*]), 4.05 (dd, J = 8.5, 8.5 Hz, 0.3H, [*trans*]), 4.93 (dd, J = 10.0, 1.8 Hz, 0.7H, [*cis*]), 4.95 (dd, J = 10.0, 1.6 Hz, 0.3H, [*cis*]), 5.01 (dd, J = 17.0, 1.8 Hz, 0.7H, [*cis*]), 5.04 (dd, J = 17.0, 1.6 Hz, 0.3H, [*trans*]), 5.07 (d, J = 5.2 Hz, 0.3H, [*trans*]), 5.09 (dd, J = 5.9, 2.9 Hz, 0.7H, [*cis*]), 5.65 (ddd, J = 17.0,

10.0, 8.5 Hz, 0.3H, [*trans*]), 5.81 (ddd, J= 17.0, 10.0, 8.8 Hz, 0.7H, [*cis*]).

^{13}C NMR (101 MHz, CDCl_3) δ 13.79, 19.28 [*trans*], 19.30 [*cis*], 31.73 [*trans*], 31.76 [*cis*], 39.21 [*cis*], 39.40 [*trans*], 41.42 [*trans*], 43.04 [*cis*], 66.95 [*trans*], 67.36 [*cis*], 70.82 [*cis*], 71.69 [*trans*], 103.98 [*trans*], 104.45 [*cis*], 115.12 [*trans*], 115.30 [*cis*], 138.82 [*cis*], 139.09 [*trans*].

FTIR (neat, cm^{-1}) : 3081, 2960, 2880, 1643, 1347, 1098, 917, 665.

GCMS m/e 170 (M^+).

2D-NOESY Experiment of *cis*- and *trans*-**3g**.

The 400 MHz proton NMR spectra were acquired in 5 mm tubes on approximately 2 wt% solutions in CDCl_3 on a Varian Unity Plus instrument using a Varian PFD Indirect Probe. As shown below, the H-4 proton of *cis* isomer **3g** showed a correlation with *cis* proton of H-3. The proton H-3 also indicated a correlation with the adjacent H-2 proton. In the case of *trans*-**3g**, the H-4 proton similarly showed a correlation with *cis* proton of H-3, but no correlation was observed between this H-3 proton and the adjacent H-2 proton. These facts allowed us to assign the *cis/trans* configuration of **3g** successfully. The 2D-NOESY spectrum obtained is shown in Figure S-1 (see next page).

exp2 noesy

SAMPLE		DEC. & VT		ACQUISITION ARRAYS	
date	Feb 24 00	dfrq	399.913	array	phase
solvent	CDC13	dn	H1	arraydim	512
file	/export/home/~dpwr	dpwr	30		phase
vmr1/vmr2/vmr3/data~		dof	0	1	1
/Hosokawa/Minami/0~		dm	0	1	1
20525Minami/021004~		dmm	C	2	2
_koga/000224-noesy~		dmf	200		
ACQUISITION	.f1d	dseq			
399.912		dres	1.0		
homo	n	PROCESSING			
HI		gf	0.078		
at	0.169	gfs	not used		
np	1024	wtfile			
sw	3034.4	proc			
fb	2000	fn	ft		
bs	4	fn	1024		
ss	8	math	f		
tpwr	45	werr			
pw	10.5	wexp			
dd	1.475	wbs			
presat	0	wnt			
mix	1.200	2D PROCESSING			
nt	-763.1	gf1	0.037		
ct	32	gfs1	not used		
atlock	n	wtfile1			
gain	32	procl	ft		
FLAGS		fn1	1024		
il	y				
in	n				
dp	y				
hs	yn				
ssssupl	n				
2D ACQUISITION					
sw1	3034.4				
ni	256				
phase	arrayed				
DISPLAY					
sdp	324.6				
wp	2019.0				
vs	500				
sc	0				
wc	130				
h2mm	15.53				
is	33.57				
rf1	263.2				
irfp	0				
th	3				
ins	100.000				
ai					
ph					
2D DISPLAY					
sp1	324.6				
wp1	2042.8				
sc2	0				
wc2	130				
rf11	263.2				
irfp1	0				

trans-3H α

trans-3H β

cis-3H α

cis-3g

trans-4H β

trans-3H β

Figure S-1. 2D-NOESY of compound **3g**

X-Ray Structure Analysis of **3c** and **3e**.

X-ray analysis were performed on Rigaku AFC7R diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$) and 12 kW rotating anode generator. Cell constants and orientation matrixes for data collection were obtained from least-square refinements using the setting angles of 20 carefully centered reflections corresponding to each cell system and dimensions. All calculations were performed using the *teXsan* crystallographic software package of Molecular Structure Corporation. The structures were solved by direct method (SIR88 or SIR92) and expanded using Fourier techniques. Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in F^2 calc; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley. The values for the mass attenuation coefficients are those of Creagh and Hubbel. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the calculation with isotropic temperature parameter on calculated positions riding on their carrier atoms.

Preparation of **3c** was described previously on page S4. Single crystals of **3c** was obtained by recrystallization from hexane and EtOAc (5:1).

Preparation of (*R,R)**3e**** was described previously on page S6. Single crystals of (*R,R**)**3e** was obtained by recrystallization from hexane and diethyl ether (3:1).

Table S-1. Crystal data and structure refinement for **3c**.

Figure S-2. ORTEP drawing of compound **3c**.

A. Crystal Data

Empirical Formula

Formula Weight

249.27

Crystal Color, Habit	yellow, plate
Crystal Dimensions	0.30 × 0.26 × 0.17 mm ³
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for Unit	
Cell Determination (2θ range)	25 (25.9 - 28.6°)
Omega Scan Peak Width at Half-height	0.33°
Lattice Parameters	a = 11.014(1) Å α = 95.35(1)° b = 13.147(2) Å β = 97.18(1)° c = 4.8355(6) Å γ = 113.337(8)°
Volume	630.0(1) Å ³
Space Group	P-1 (#2)
Z value	2
D _{calc}	1.314 g/cm ³
F(000)	264.00
μ(MoKα)	0.98 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku AFC7R (rotating anode)
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factor = 7.40)
Temperature	23.0 °C
Voltage, Current	50 kV, 250 mA
Collimator Size	0.5 mm
Take-off Angle	6.0°
Detector Aperture	3.0 mm horizontal 4.0 mm vertical
Crystal to Detector Distance	235 mm
Scan Type	ω-2θ
Scan Rate	4.0°/min (in ω) (up to 5 scans)
Scan Width	(1.84 + 0.30 tanθ)°
2θ _{max}	55.0°
No. of Reflections Measured	Total: 3042

	Unique: 2891 ($R_{\text{int}} = 0.007$)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.9064 - 0.9982)
	Secondary Extinction
	(coefficient: 3.71810e-07)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR88)
Refinement	Full-matrix least-squares
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$1/\sigma^2(F_o^2)$
p-factor	0.0700
Anomalous Dispersion	All non-hydrogen atoms
No. of Reflections (All, $2\sigma < 55.00^\circ$)	2891
No. Variables	164
Reflection/Parameter Ratio	17.63
Residuals: R; Rw	0.073 ; 0.206
Residuals: R1	0.061
No. of Reflections to calc R1	1512
Goodness of Fit Indicator	1.50
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	$0.64 \text{ e}^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	$-0.29 \text{ e}^-/\text{\AA}^3$

Table S-2. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}
O(1)	0.6603(2)	0.5439(2)	-0.1830(5)	8.16(7)
O(2)	0.8724(2)	0.5839(2)	-0.1017(5)	7.74(7)
O(3)	0.9013(2)	0.0825(2)	0.8647(5)	7.83(6)
O(4)	0.7393(2)	-0.0887(2)	0.6318(4)	6.18(5)
N(1)	0.7563(3)	0.5281(2)	-0.0719(5)	5.91(6)
C(1)	0.7317(2)	0.4413(2)	0.1062(5)	4.83(6)

C(2)	0.6022(3)	0.3813(3)	0.1516(7)	5.84(7)
C(3)	0.5805(2)	0.2991(3)	0.3152(6)	5.70(7)
C(4)	0.6840(2)	0.2727(2)	0.4406(5)	4.65(5)
C(5)	0.8135(2)	0.3362(2)	0.3886(6)	5.46(6)
C(6)	0.8367(2)	0.4185(2)	0.2244(6)	5.49(6)
C(7)	0.6513(2)	0.1841(2)	0.6099(6)	5.11(6)
C(8)	0.7265(3)	0.1347(2)	0.7265(5)	5.08(6)
C(9)	0.8703(3)	0.1586(2)	0.7116(6)	5.77(7)
C(10)	0.6787(3)	0.0404(2)	0.8933(6)	5.92(7)
C(11)	0.7816(3)	-0.0072(3)	0.8871(7)	6.48(8)
C(12)	0.8257(3)	-0.1437(3)	0.5962(7)	6.98(9)
C(13)	0.7585(4)	-0.2438(3)	0.3776(8)	7.68(10)
H(1)	0.5289	0.3976	0.0677	7.0
H(2)	0.4911	0.2593	0.3524	6.9
H(3)	0.8874	0.3209	0.4729	6.5
H(4)	0.9260	0.4613	0.1941	6.6
H(5)	0.5605	0.1558	0.6464	6.0
H(6)	0.9291	0.2342	0.7916	7.0

Table S-3. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B _{eq}
H(7)	0.8823	0.1464	0.5193	7.0
H(8)	0.6720	0.0658	1.0809	7.0
H(9)	0.5895	-0.0152	0.8049	7.0
H(10)	0.7934	-0.0408	1.0552	8.2
H(11)	0.9089	-0.0943	0.5485	8.5
H(12)	0.8500	-0.1668	0.7746	8.5
H(13)	0.6771	-0.2937	0.4295	9.3
H(14)	0.7360	-0.2211	0.2034	9.3
H(15)	0.8140	-0.2823	0.3526	9.3

$$B_{eq} = \frac{8}{3} \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \theta + 2U_{13}(aa^*cc^*)\cos \theta + 2U_{23}(bb^*cc^*)\cos \theta)$$

Table S-4. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O(1)	0.086(2)	0.108(2)	0.126(2)	0.051(1)	0.005(1)	0.024(2)
O(2)	0.075(1)	0.081(1)	0.140(2)	0.030(1)	0.030(1)	0.025(1)
O(3)	0.071(1)	0.095(2)	0.111(2)	0.021(1)	-0.017(1)	0.021(1)
O(4)	0.071(1)	0.078(1)	0.078(1)	0.0309(10)	-0.0039(9)	-0.0054(10)
N(1)	0.069(2)	0.068(1)	0.088(2)	0.035(1)	0.007(1)	-0.006(1)
C(1)	0.052(1)	0.057(1)	0.070(2)	0.023(1)	0.006(1)	-0.008(1)
C(2)	0.048(1)	0.079(2)	0.097(2)	0.032(1)	0.008(1)	0.001(2)
C(3)	0.042(1)	0.078(2)	0.092(2)	0.023(1)	0.014(1)	-0.002(2)
C(4)	0.043(1)	0.064(2)	0.062(1)	0.019(1)	0.0072(10)	-0.011(1)
C(5)	0.042(1)	0.073(2)	0.087(2)	0.021(1)	0.007(1)	0.007(2)
C(6)	0.042(1)	0.069(2)	0.090(2)	0.018(1)	0.009(1)	0.001(2)
C(7)	0.047(1)	0.065(2)	0.071(2)	0.014(1)	0.018(1)	-0.011(1)
C(8)	0.055(1)	0.072(2)	0.054(1)	0.019(1)	0.007(1)	-0.011(1)
C(9)	0.052(1)	0.075(2)	0.081(2)	0.020(1)	-0.003(1)	0.005(1)
C(10)	0.084(2)	0.071(2)	0.062(2)	0.022(1)	0.024(1)	-0.001(1)
C(11)	0.074(2)	0.072(2)	0.085(2)	0.019(2)	-0.004(1)	0.012(2)
C(12)	0.065(2)	0.108(3)	0.096(2)	0.041(2)	0.013(2)	0.006(2)
C(13)	0.096(2)	0.082(2)	0.122(3)	0.039(2)	0.041(2)	0.010(2)

The general temperature factor expression:

$$\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table S-5. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
O(1)	N(1)	1.226(3)	O(2)	N(1)	1.232(3)
O(3)	C(9)	1.418(4)	O(3)	C(11)	1.403(4)
O(4)	C(11)	1.451(4)	O(4)	C(12)	1.422(4)
N(1)	C(1)	1.454(4)	C(1)	C(2)	1.387(4)
C(1)	C(6)	1.377(3)	C(2)	C(3)	1.361(4)
C(2)	H(1)	0.97	C(3)	C(4)	1.403(4)

C(3)	H(2)	0.96	C(4)	C(5)	1.407(3)
C(4)	C(7)	1.441(4)	C(5)	C(6)	1.363(4)
C(5)	H(3)	0.97	C(6)	H(4)	0.96
C(7)	C(8)	1.343(4)	C(7)	H(5)	0.97
C(8)	C(9)	1.500(4)	C(8)	C(10)	1.497(4)
C(9)	H(6)	0.96	C(9)	H(7)	0.96
C(10)	C(11)	1.498(4)	C(10)	H(8)	0.96
C(10)	H(9)	0.97	C(11)	H(10)	0.98
C(12)	C(13)	1.473(5)	C(12)	H(11)	0.96
C(12)	H(12)	0.98	C(13)	H(13)	0.96
C(13)	H(14)	0.96	C(13)	H(15)	0.95

Table S-6. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(9)	O(3)	C(11)	109.3(2)	C(11)	O(4)	C(12)	114.4(2)
O(1)	N(1)	O(2)	122.6(3)	O(1)	N(1)	C(1)	118.4(2)
O(2)	N(1)	C(1)	119.0(2)	N(1)	C(1)	C(2)	119.5(2)
N(1)	C(1)	C(6)	119.7(2)	C(2)	C(1)	C(6)	120.8(3)
C(1)	C(2)	C(3)	118.9(2)	C(1)	C(2)	H(1)	120.4
C(3)	C(2)	H(1)	120.8	C(2)	C(3)	C(4)	122.6(2)
C(2)	C(3)	H(2)	118.8	C(4)	C(3)	H(2)	118.6
C(3)	C(4)	C(5)	116.3(3)	C(3)	C(4)	C(7)	118.7(2)
C(5)	C(4)	C(7)	125.0(2)	C(4)	C(5)	C(6)	121.7(2)
C(4)	C(5)	H(3)	118.7	C(6)	C(5)	H(3)	119.6
C(1)	C(6)	C(5)	119.8(2)	C(1)	C(6)	H(4)	120.1
C(5)	C(6)	H(4)	120.1	C(4)	C(7)	C(8)	130.7(2)
C(4)	C(7)	H(5)	114.7	C(8)	C(7)	H(5)	114.6
C(7)	C(8)	C(9)	128.2(3)	C(7)	C(8)	C(10)	125.4(2)
C(9)	C(8)	C(10)	106.4(3)	O(3)	C(9)	C(8)	106.0(2)
O(3)	C(9)	H(6)	110.5	O(3)	C(9)	H(7)	109.6
C(8)	C(9)	H(6)	111.7	C(8)	C(9)	H(7)	111.1
H(6)	C(9)	H(7)	108.0	C(8)	C(10)	C(11)	103.1(2)
C(8)	C(10)	H(8)	111.9	C(8)	C(10)	H(9)	110.9
C(11)	C(10)	H(8)	113.1	C(11)	C(10)	H(9)	111.3

H(8)	C(10)	H(9)	106.7	O(3)	C(11)	O(4)	108.5(3)
O(3)	C(11)	C(10)	105.9(3)	O(3)	C(11)	H(10)	111.1
O(4)	C(11)	C(10)	107.2(2)	O(4)	C(11)	H(10)	111.4
C(10)	C(11)	H(10)	112.5	O(4)	C(12)	C(13)	110.4(3)

Table S-7. Bond Angles(°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
O(4)	C(12)	H(11)	111.4	O(4)	C(12)	H(12)	109.8
C(13)	C(12)	H(11)	110.1	C(13)	C(12)	H(12)	109.0
H(11)	C(12)	H(12)	106.0	C(12)	C(13)	H(13)	109.5
C(12)	C(13)	H(14)	108.9	C(12)	C(13)	H(15)	111.7
H(13)	C(13)	H(14)	108.4	H(13)	C(13)	H(15)	109.0
H(14)	C(13)	H(15)	109.2				

Table S-8. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(1)	N(1)	C(1)	C(2)	-1.7(4)	O(1)	N(1)	C(1)	C(6)	177.3(2)
O(2)	N(1)	C(1)	C(2)	177.2(2)	O(2)	N(1)	C(1)	C(6)	-3.8(4)
O(3)	C(9)	C(8)	C(7)	-179.0(2)	O(3)	C(9)	C(8)	C(10)	-0.6(3)
O(3)	C(11)	O(4)	C(12)	67.2(3)	O(3)	C(11)	C(10)	C(8)	28.9(3)
O(4)	C(11)	O(3)	C(9)	83.7(3)	O(4)	C(11)	C(10)	C(8)	-86.7(3)
N(1)	C(1)	C(2)	C(3)	179.0(2)	N(1)	C(1)	C(6)	C(5)	-179.2(2)
C(1)	C(2)	C(3)	C(4)	0.1(4)	C(1)	C(6)	C(5)	C(4)	0.3(4)
C(2)	C(1)	C(6)	C(5)	-0.2(4)	C(2)	C(3)	C(4)	C(5)	0.0(4)
C(2)	C(3)	C(4)	C(7)	-179.8(3)	C(3)	C(2)	C(1)	C(6)	0.0(4)
C(3)	C(4)	C(5)	C(6)	-0.2(4)	C(3)	C(4)	C(7)	C(8)	172.0(2)
C(4)	C(7)	C(8)	C(9)	-0.2(4)	C(4)	C(7)	C(8)	C(10)	-178.3(2)
C(5)	C(4)	C(7)	C(8)	-7.8(4)	C(6)	C(5)	C(4)	C(7)	179.6(3)
C(7)	C(8)	C(10)	C(11)	161.6(2)	C(8)	C(9)	O(3)	C(11)	19.7(3)
C(9)	O(3)	C(11)	C(10)	-31.0(3)	C(9)	C(8)	C(10)	C(11)	-16.9(3)
C(10)	C(11)	O(4)	C(12)	-178.8(2)	C(11)	O(4)	C(12)	C(13)	165.1(3)

Table S-9. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	atom	atom	distance
O(1)	H(1) ¹⁾	2.59	O(1)	H(13) ²⁾	2.94
O(1)	H(15) ³⁾	3.09	O(1)	H(14) ³⁾	3.20
O(1)	C(2) ¹⁾	3.419(3)	O(1)	H(13) ³⁾	3.43
O(1)	C(13) ³⁾	3.431(4)	O(1)	H(15) ²⁾	3.46
O(1)	C(2) ⁴⁾	3.529(4)	O(1)	C(13) ²⁾	3.573(5)
O(1)	C(3) ⁴⁾	3.575(4)	O(1)	H(12) ²⁾	3.58
O(2)	H(4) ⁵⁾	2.59	O(2)	H(6) ⁶⁾	2.67
O(2)	H(15) ³⁾	2.98	O(2)	H(3) ⁵⁾	3.28
O(2)	C(6) ⁵⁾	3.342(3)	O(2)	H(15) ²⁾	3.44
O(2)	H(12) ²⁾	3.48	O(2)	H(3) ⁶⁾	3.53
O(2)	C(9) ⁶⁾	3.595(4)	O(3)	H(12) ⁷⁾	2.80
O(3)	H(11) ⁸⁾	3.04	O(3)	H(7) ⁹⁾	3.25
O(3)	H(11) ⁷⁾	3.26	O(3)	C(12) ⁷⁾	3.495(4)
O(3)	H(15) ⁸⁾	3.56	O(3)	H(10) ⁷⁾	3.60
O(4)	H(2) ¹⁰⁾	2.66	O(4)	H(10) ⁴⁾	2.99
O(4)	H(5) ¹⁰⁾	3.14	O(4)	H(14) ⁹⁾	3.40
O(4)	C(3) ¹⁰⁾	3.573(3)	N(1)	H(15) ³⁾	2.88
N(1)	C(13) ³⁾	3.526(4)	N(1)	H(14) ³⁾	3.54
N(1)	H(4) ⁵⁾	3.57	C(1)	H(15) ³⁾	3.43
C(1)	C(4) ⁴⁾	3.588(3)	C(2)	H(5) ⁴⁾	3.50
C(2)	H(14) ¹¹⁾	3.57	C(3)	H(13) ¹⁰⁾	3.21
C(3)	H(9) ¹⁰⁾	3.40	C(3)	H(5) ⁴⁾	3.52
C(4)	H(8) ⁴⁾	3.04	C(4)	H(9) ¹⁰⁾	3.50
C(5)	H(4) ⁶⁾	3.30	C(5)	H(8) ⁴⁾	3.37

Table S-10. Non-bonded Contacts out to 3.60 Å (continued)

atom	atom	distance	atom	atom	distance
C(6)	H(4) ⁶⁾	3.36	C(6)	H(4) ⁵⁾	3.47
C(6)	H(3) ⁶⁾	3.58	C(6)	H(6) ⁴⁾	3.58
C(7)	H(8) ⁴⁾	2.95	C(7)	H(9) ¹⁰⁾	3.03

C(8)	H(8) ⁴	3.08	C(9)	H(11) ⁸	3.23
C(9)	H(15) ⁸	3.27	C(9)	H(8) ⁴	3.33
C(10)	H(7) ⁹	3.34	C(10)	H(9) ¹²	3.37
C(10)	H(5) ¹⁰	3.47	C(10)	H(8) ¹²	3.57
C(11)	H(14) ⁹	3.22	C(11)	H(7) ⁹	3.30
C(11)	H(2) ¹⁰	3.45	C(12)	H(10) ⁴	3.10
C(12)	H(2) ¹⁰	3.26	C(12)	H(14) ⁹	3.33
C(12)	H(7) ⁸	3.35	C(12)	H(11) ⁸	3.54
C(13)	H(2) ¹⁰	3.13	C(13)	H(10) ⁴	3.13
C(13)	H(12) ⁴	3.32	C(13)	H(1) ¹¹	3.34
C(13)	H(6) ⁸	3.59	C(13)	H(7) ⁸	3.59
H(1)	H(13) ¹¹	2.89	H(1)	H(14) ¹¹	2.95
H(1)	H(1) ¹	3.11	H(1)	H(13) ¹⁰	3.53
H(2)	H(13) ¹⁰	2.41	H(2)	H(9) ¹⁰	2.96
H(2)	H(14) ¹¹	3.29	H(2)	H(12) ¹⁰	3.41
H(2)	H(14) ¹⁰	3.42	H(2)	H(10) ¹⁰	3.50
H(3)	H(4) ⁶	2.94	H(3)	H(8) ⁴	3.44
H(3)	H(6) ⁴	3.53	H(3)	H(15) ⁸	3.53
H(4)	H(4) ⁵	2.65	H(4)	H(4) ⁶	3.06
H(4)	H(6) ⁴	3.42	H(5)	H(9) ¹⁰	2.61
H(5)	H(8) ⁴	3.43	H(5)	H(8) ¹²	3.53

Table S-11. Non-bonded Contacts out to 3.60 Å (continued)

atom	atom	distance	atom	atom	distance
H(5)	H(9) ¹²	3.57	H(6)	H(15) ⁸	2.84
H(6)	H(12) ⁷	3.45	H(6)	H(11) ⁸	3.47
H(7)	H(11) ⁸	2.70	H(7)	H(8) ⁴	2.72
H(7)	H(10) ⁴	2.93	H(7)	H(15) ⁸	3.05
H(7)	H(12) ⁸	3.36	H(8)	H(9) ¹²	2.83
H(8)	H(8) ¹²	3.43	H(9)	H(9) ¹²	3.00
H(9)	H(9) ¹⁰	3.48	H(10)	H(14) ⁹	2.40
H(10)	H(11) ⁹	2.84	H(10)	H(11) ⁷	3.28
H(11)	H(11) ⁸	2.63	H(12)	H(14) ⁹	2.57
H(12)	H(15) ⁹	3.30			

Symmetry operations

(1)	-X+1,-Y+1,-Z	(2)	X,Y+1,Z-1
(3)	X,Y+1,Z	(4)	X,Y,Z-1
(5)	-X+2,-Y+1,-Z	(6)	-X+2,-Y+1,-Z+1
(7)	-X+2,-Y,-Z+2	(8)	-X+2,-Y,-Z+1
(9)	X,Y,Z+1	(10)	-X+1,-Y,-Z+1
(11)	-X+1,-Y,-Z	(12)	-X+1,-Y,-Z+2

Table S-12. Crystal data and structure refinement for R^*R^* **3e**.

Figure S-3. ORTEP drawing of compound **3e**.

A. Crystal Data

Empirical Formula	$C_{16}H_{19}NO_5$
Formula Weight	305.33
Crystal Color, Habit	pale_yellow, rectangular
Crystal Dimensions	0.25 X 0.15 X 0.15 mm
Crystal System	monoclinic
Lattice Type	C-centered
No. of Reflections Used for Unit	
Cell Determination (2 θ range)	25 (22.1 - 23.8°)
Omega Scan Peak Width	
at Half-height	0.34°
Lattice Parameters	a = 19.238(4) Å
	b = 12.755(3) Å β = 124.62(1)°
	c = 15.148(3) Å
Volume	3058(1) Å ³
Space Group	C2/c (#15)
Z value	8

D _{calc}	1.326 g/cm ³
F(000)	1296.00
m(MoKα)	0.99 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku AFC7R (rotating anode)
Radiation	MoKα ($\lambda = 0.71069 \text{ \AA}$) graphite monochromated
Attenuator	Zr foil (factor = 7.40)
Temperature	25.0 °C
Voltage, Current	50 kV, 250 mA
Collimator Size	0.5 mm
Take-off Angle	6.0°
Detector Aperture	3.0 mm horizontal 6.5 mm vertical
Crystal to Detector Distance	235 mm
Scan Type	ω -2 θ
Scan Rate	8.0°/min (in ω) (up to 5 scans)
Scan Width	(1.52 + 0.30 tan θ)°
2 θ_{max}	55.0°
No. of Reflections Measured	Total: 3516 Unique: 3259 ($R_{\text{int}} = 0.048$)
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$1/s^2(F_o^2)$
p-factor	0.0350
Anomalous Dispersion	All non-hydrogen atoms
No. of Reflections (All, 2 $\theta < 54.99^\circ$)	3259
No. Variables	199
Reflection/Parameter Ratio	16.38

Residuals: R; Rw	0.147 ; 0.163
Residuals: R1	0.052
No. of Reflections to calc R1	842
Goodness of Fit Indicator	0.99
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.69 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.70 e ⁻ /Å ³

Table S-13. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B _{eq}
O(1)	0.5013(3)	0.8420(3)	0.1224(4)	10.7(1)
O(2)	0.6239(3)	0.8177(3)	0.1566(4)	9.6(1)
O(3)	0.6824(2)	0.1562(2)	0.2181(2)	5.34(8)
O(4)	0.6412(2)	0.1065(2)	0.3312(2)	4.87(7)
O(5)	0.7465(2)	-0.0225(3)	0.4049(2)	5.76(9)
N(1)	0.5575(4)	0.7838(4)	0.1399(4)	7.1(1)
C(1)	0.5268(3)	0.4544(4)	0.1369(4)	4.82(10)
C(2)	0.4616(3)	0.5226(4)	0.1115(4)	6.2(1)
C(3)	0.4711(3)	0.6298(4)	0.1129(4)	6.3(1)
C(4)	0.5460(3)	0.6712(4)	0.1394(4)	5.3(1)
C(5)	0.6127(3)	0.6059(4)	0.1656(4)	5.7(1)
C(6)	0.6031(3)	0.4986(4)	0.1640(4)	5.0(1)
C(7)	0.5117(3)	0.3423(4)	0.1330(4)	5.0(1)
C(8)	0.6246(3)	0.0970(4)	0.2271(3)	5.2(1)
C(9)	0.5397(3)	0.1482(4)	0.1490(4)	5.6(1)
C(10)	0.5627(3)	0.2612(4)	0.1556(3)	4.55(9)
C(11)	0.6549(3)	0.2631(4)	0.1976(4)	4.84(10)
C(12)	0.7247(3)	0.0789(4)	0.4164(4)	5.14(10)
C(13)	0.7306(3)	0.0946(4)	0.5195(3)	5.6(1)
C(14)	0.6860(3)	0.0079(4)	0.5375(3)	5.6(1)
C(15)	0.7132(3)	-0.0979(4)	0.5227(4)	6.2(1)
C(16)	0.6999(3)	-0.1030(4)	0.4149(4)	6.0(1)
H(1)	0.4041	0.4893	0.0927	8.5
H(2)	0.4207	0.6772	0.0928	8.0

Table S-14. Atomic coordinates and B_{iso}/B_{eq} (continued)

atom	x	y	z	B _{eq}
H(3)	0.6671	0.6368	0.1849	7.3
H(4)	0.6513	0.4496	0.1819	7.0
H(5)	0.4507	0.3243	0.1049	6.9
H(6)	0.6260	0.0205	0.2080	7.6
H(7)	0.5100	0.1203	0.0756	7.2
H(8)	0.5002	0.1355	0.1696	7.2
H(9)	0.6886	0.3115	0.2613	7.4
H(10)	0.6641	0.3001	0.1449	7.4
H(11)	0.7675	0.1316	0.4202	7.4
H(12)	0.7899	0.0994	0.5835	6.8
H(13)	0.7062	0.1625	0.5192	6.8
H(14)	0.6987	0.0127	0.6086	5.9
H(15)	0.6276	0.0154	0.4868	5.9
H(16)	0.7725	-0.1098	0.5795	6.9
H(17)	0.6822	-0.1527	0.5310	6.9
H(18)	0.6409	-0.0984	0.3607	7.2
H(19)	0.7183	-0.1721	0.4073	7.2

$$B_{eq} = 8/3 \text{ PI}^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \theta + 2U_{13}(aa^*cc^*)\cos \theta + 2U_{23}(bb^*cc^*)\cos \theta)$$

Table S-15. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O(1)	0.135(4)	0.087(3)	0.177(4)	0.042(3)	0.083(4)	0.014(3)
O(2)	0.129(4)	0.089(3)	0.157(4)	-0.013(3)	0.088(4)	0.009(3)
O(3)	0.082(2)	0.068(2)	0.072(2)	-0.002(2)	0.054(2)	0.002(2)
O(4)	0.061(2)	0.072(2)	0.053(2)	0.003(2)	0.033(1)	0.005(2)
O(5)	0.066(2)	0.089(2)	0.072(2)	0.015(2)	0.044(2)	0.005(2)
N(1)	0.115(4)	0.072(3)	0.068(3)	0.006(2)	0.043(4)	-0.004(3)
C(1)	0.051(2)	0.080(3)	0.044(3)	-0.001(2)	0.022(3)	0.011(3)
C(2)	0.047(3)	0.096(3)	0.079(4)	0.005(3)	0.029(3)	0.015(4)
C(3)	0.062(3)	0.094(3)	0.077(4)	0.020(3)	0.036(3)	0.016(4)

C(4)	0.068(3)	0.076(3)	0.048(3)	0.006(2)	0.027(3)	0.001(3)
C(5)	0.064(3)	0.074(2)	0.076(3)	-0.001(3)	0.039(3)	0.015(3)
C(6)	0.048(2)	0.073(2)	0.063(3)	0.002(2)	0.028(3)	0.010(3)
C(7)	0.048(3)	0.080(2)	0.048(3)	-0.006(2)	0.018(2)	0.006(3)
C(8)	0.077(3)	0.069(3)	0.056(2)	-0.004(2)	0.041(2)	-0.004(3)
C(9)	0.068(3)	0.077(3)	0.055(3)	-0.018(3)	0.026(2)	-0.002(3)
C(10)	0.051(2)	0.078(2)	0.034(2)	-0.008(2)	0.017(2)	0.008(3)
C(11)	0.055(2)	0.070(2)	0.068(3)	0.003(3)	0.040(2)	0.008(3)
C(12)	0.054(2)	0.080(3)	0.055(2)	-0.011(3)	0.027(2)	-0.003(3)
C(13)	0.077(3)	0.078(3)	0.052(3)	0.003(3)	0.034(3)	-0.003(3)
C(14)	0.076(3)	0.087(3)	0.055(3)	0.015(3)	0.041(3)	0.014(3)
C(15)	0.082(4)	0.081(3)	0.079(3)	0.016(3)	0.051(3)	0.020(3)
C(16)	0.098(4)	0.061(3)	0.082(3)	0.009(3)	0.059(3)	0.002(3)

The general temperature factor expression:

$$\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$$

Table S-16. Bond Lengths(Å)

atom	atom	distance	atom	atom	distance
O(1)	N(1)	1.210(5)	O(2)	N(1)	1.231(5)
O(3)	C(8)	1.414(5)	O(3)	C(11)	1.432(5)
O(4)	C(8)	1.426(5)	O(4)	C(12)	1.420(5)
O(5)	C(12)	1.401(5)	O(5)	C(16)	1.427(5)
N(1)	C(4)	1.452(6)	C(1)	C(2)	1.389(6)
C(1)	C(6)	1.398(6)	C(1)	C(7)	1.454(6)
C(2)	C(3)	1.379(6)	C(2)	H(1)	1.06
C(3)	C(4)	1.364(6)	C(3)	H(2)	1.03
C(4)	C(5)	1.387(6)	C(5)	C(6)	1.379(6)
C(5)	H(3)	0.99	C(6)	H(4)	1.02
C(7)	C(10)	1.331(6)	C(7)	H(5)	1.02
C(8)	C(9)	1.516(6)	C(8)	H(6)	1.02
C(9)	C(10)	1.494(6)	C(9)	H(7)	0.98
C(9)	H(8)	0.98	C(10)	C(11)	1.506(5)

C(11)	H(9)	1.01	C(11)	H(10)	1.02
C(12)	C(13)	1.513(6)	C(12)	H(11)	1.04
C(13)	C(14)	1.516(6)	C(13)	H(12)	0.99
C(13)	H(13)	0.98	C(14)	C(15)	1.510(6)
C(14)	H(14)	0.96	C(14)	H(15)	0.94
C(15)	C(16)	1.504(7)	C(15)	H(16)	0.98
C(15)	H(17)	0.97	C(16)	H(18)	0.95
C(16)	H(19)	0.98			

Table S-17. Bond Angles(°)

atom	atom	atom	angle	atom	atom	atom	angle
C(8)	O(3)	C(11)	108.4(3)	C(8)	O(4)	C(12)	114.3(3)
C(12)	O(5)	C(16)	113.6(3)	O(1)	N(1)	O(2)	121.5(6)
O(1)	N(1)	C(4)	119.4(6)	O(2)	N(1)	C(4)	119.1(6)
C(2)	C(1)	C(6)	117.5(5)	C(2)	C(1)	C(7)	118.4(4)
C(6)	C(1)	C(7)	124.1(5)	C(1)	C(2)	C(3)	121.7(5)
C(1)	C(2)	H(1)	117.6	C(3)	C(2)	H(1)	120.6
C(2)	C(3)	C(4)	119.8(5)	C(2)	C(3)	H(2)	118.9
C(4)	C(3)	H(2)	121.2	N(1)	C(4)	C(3)	121.1(5)
N(1)	C(4)	C(5)	118.7(5)	C(3)	C(4)	C(5)	120.2(5)
C(4)	C(5)	C(6)	119.9(5)	C(4)	C(5)	H(3)	119.6
C(6)	C(5)	H(3)	120.5	C(1)	C(6)	C(5)	120.9(5)
C(1)	C(6)	H(4)	118.4	C(5)	C(6)	H(4)	120.7
C(1)	C(7)	C(10)	130.7(4)	C(1)	C(7)	H(5)	113.2
C(10)	C(7)	H(5)	115.9	O(3)	C(8)	O(4)	111.5(4)
O(3)	C(8)	C(9)	104.7(4)	O(3)	C(8)	H(6)	109.5
O(4)	C(8)	C(9)	106.9(4)	O(4)	C(8)	H(6)	111.7
C(9)	C(8)	H(6)	112.4	C(8)	C(9)	C(10)	102.5(4)
C(8)	C(9)	H(7)	113.7	C(8)	C(9)	H(8)	111.4
C(10)	C(9)	H(7)	112.6	C(10)	C(9)	H(8)	113.1
H(7)	C(9)	H(8)	104.0	C(7)	C(10)	C(9)	125.8(4)
C(7)	C(10)	C(11)	128.0(4)	C(9)	C(10)	C(11)	106.2(4)
O(3)	C(11)	C(10)	106.1(4)	O(3)	C(11)	H(9)	114.6
O(3)	C(11)	H(10)	113.7	C(10)	C(11)	H(9)	112.1

C(10)	C(11)	H(10)	111.1	H(9)	C(11)	H(10)	99.3
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Table S-18. Bond Angles (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
O(4)	C(12)	O(5)	112.3(4)	O(4)	C(12)	C(13)	106.8(4)
O(4)	C(12)	H(11)	110.0	O(5)	C(12)	C(13)	113.5(4)
O(5)	C(12)	H(11)	108.6	C(13)	C(12)	H(11)	105.5
C(12)	C(13)	C(14)	111.8(4)	C(12)	C(13)	H(12)	112.7
C(12)	C(13)	H(13)	110.8	C(14)	C(13)	H(12)	108.9
C(14)	C(13)	H(13)	109.0	H(12)	C(13)	H(13)	103.3
C(13)	C(14)	C(15)	110.3(4)	C(13)	C(14)	H(14)	110.3
C(13)	C(14)	H(15)	108.4	C(15)	C(14)	H(14)	109.5
C(15)	C(14)	H(15)	108.8	H(14)	C(14)	H(15)	109.4
C(14)	C(15)	C(16)	109.9(4)	C(14)	C(15)	H(16)	109.8
C(14)	C(15)	H(17)	109.6	C(16)	C(15)	H(16)	110.0
C(16)	C(15)	H(17)	111.7	H(16)	C(15)	H(17)	105.7
O(5)	C(16)	C(15)	110.8(4)	O(5)	C(16)	H(18)	112.1
O(5)	C(16)	H(19)	110.1	C(15)	C(16)	H(18)	108.5
C(15)	C(16)	H(19)	108.5	H(18)	C(16)	H(19)	106.7

Table S-19. Torsion Angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
O(1)	N(1)	C(4)	C(3)	4.2(8)	O(1)	N(1)	C(4)	C(5)	-176.4(5)
O(2)	N(1)	C(4)	C(3)	-174.7(5)	O(2)	N(1)	C(4)	C(5)	4.7(7)
O(3)	C(8)	O(4)	C(12)	-55.8(5)	O(3)	C(8)	C(9)	C(10)	-33.9(4)
O(3)	C(11)	C(10)	C(7)	174.5(4)	O(3)	C(11)	C(10)	C(9)	-2.5(5)
O(4)	C(8)	O(3)	C(11)	-81.2(4)	O(4)	C(8)	C(9)	C(10)	84.5(4)
O(4)	C(12)	O(5)	C(16)	-67.0(5)	O(4)	C(12)	C(13)	C(14)	75.3(5)
O(5)	C(12)	O(4)	C(8)	-55.4(5)	O(5)	C(12)	C(13)	C(14)	-49.0(5)
O(5)	C(16)	C(15)	C(14)	58.7(5)	N(1)	C(4)	C(3)	C(2)	179.0(5)
N(1)	C(4)	C(5)	C(6)	-178.9(4)	C(1)	C(2)	C(3)	C(4)	0.2(8)
C(1)	C(6)	C(5)	C(4)	-0.5(7)	C(1)	C(7)	C(10)	C(9)	179.6(5)

C(1)	C(7)	C(10)	C(11)	3.2(8)	C(2)	C(1)	C(6)	C(5)	0.3(7)
C(2)	C(1)	C(7)	C(10)	-178.2(5)	C(2)	C(3)	C(4)	C(5)	-0.4(8)
C(3)	C(2)	C(1)	C(6)	-0.2(8)	C(3)	C(2)	C(1)	C(7)	-179.7(5)
C(3)	C(4)	C(5)	C(6)	0.6(7)	C(5)	C(6)	C(1)	C(7)	179.8(5)
C(6)	C(1)	C(7)	C(10)	2.2(8)	C(7)	C(10)	C(9)	C(8)	-155.3(4)
C(8)	O(3)	C(11)	C(10)	-19.8(4)	C(8)	O(4)	C(12)	C(13)	179.6(4)
C(8)	C(9)	C(10)	C(11)	21.8(5)	C(9)	C(8)	O(3)	C(11)	34.0(4)
C(9)	C(8)	O(4)	C(12)	-169.6(4)	C(12)	O(5)	C(16)	C(15)	-59.2(5)
C(12)	C(13)	C(14)	C(15)	49.1(5)	C(13)	C(12)	O(5)	C(16)	54.2(5)
C(13)	C(14)	C(15)	C(16)	-54.1(5)					

Table S-20. Non-bonded Contacts out to 3.60 Å

atom	atom	distance	atom	atom	distance
O(1)	H(7) ¹⁾	2.92	O(1)	H(17) ²⁾	2.92
O(1)	H(18) ²⁾	2.99	O(1)	H(6) ³⁾	3.01
O(1)	H(15) ²⁾	3.02	O(1)	H(18) ³⁾	3.13
O(1)	C(15) ²⁾	3.484(7)	O(2)	H(6) ³⁾	2.69
O(2)	H(14) ⁴⁾	2.91	O(2)	H(7) ¹⁾	3.06
O(2)	H(9) ⁵⁾	3.08	O(2)	H(18) ³⁾	3.11
O(2)	H(19) ³⁾	3.15	O(2)	H(13) ⁴⁾	3.26
O(2)	H(15) ⁴⁾	3.37	O(2)	H(10) ⁵⁾	3.43
O(2)	C(16) ³⁾	3.461(7)	O(2)	C(14) ⁴⁾	3.475(6)
O(2)	C(11) ⁵⁾	3.577(6)	O(3)	H(3) ⁶⁾	2.40
O(3)	H(17) ⁷⁾	2.83	O(3)	H(14) ⁷⁾	2.84
O(3)	C(5) ⁶⁾	3.340(6)	O(3)	C(15) ⁷⁾	3.413(5)
O(3)	H(16) ⁷⁾	3.45	O(3)	C(14) ⁷⁾	3.476(5)
O(4)	H(8) ⁸⁾	2.74	O(5)	H(1) ⁹⁾	2.77
O(5)	H(4) ⁶⁾	2.94	O(5)	H(10) ⁶⁾	3.18
O(5)	H(3) ⁶⁾	3.36	O(5)	C(2) ⁹⁾	3.494(5)
O(5)	H(2) ⁹⁾	3.52	N(1)	H(7) ¹⁾	3.00
N(1)	H(18) ³⁾	3.15	N(1)	H(6) ³⁾	3.22
N(1)	H(19) ³⁾	3.47	C(1)	H(1) ⁸⁾	3.54
C(2)	H(12) ¹⁰⁾	3.45	C(2)	H(16) ¹⁰⁾	3.56
C(2)	C(2) ⁸⁾	3.57(1)	C(3)	H(10) ¹⁾	3.36

C(3)	H(16) ¹⁰	3.57	C(5)	H(16) ¹¹	3.18
C(5)	H(11) ⁵	3.24	C(6)	H(12) ¹¹	3.39
C(6)	H(14) ¹¹	3.39	C(6)	H(16) ¹¹	3.50

Table S-21. Non-bonded Contacts out to 3.60 Å (continued)

atom	atom	distance	atom	atom	distance
C(8)	H(14) ⁷	3.18	C(8)	H(3) ⁶	3.47
C(8)	H(8) ⁸	3.57	C(9)	H(15) ⁸	3.15
C(9)	H(8) ⁸	3.25	C(11)	H(17) ⁷	3.18
C(11)	H(3) ⁶	3.25	C(11)	H(12) ¹¹	3.35
C(12)	H(1) ⁹	3.05	C(12)	H(3) ⁶	3.30
C(12)	H(13) ¹¹	3.48	C(13)	H(9) ¹¹	3.00
C(13)	H(1) ⁹	3.05	C(13)	H(13) ¹¹	3.50
C(14)	H(6) ¹²	3.39	C(14)	H(7) ⁸	3.44
C(14)	H(9) ¹¹	3.47	C(14)	H(8) ⁸	3.54
C(15)	H(19) ¹³	3.14	C(15)	H(1) ⁹	3.48
C(15)	H(2) ¹⁴	3.58	C(15)	H(10) ¹²	3.60
C(16)	H(10) ⁶	3.45	C(16)	H(1) ⁹	3.57
C(16)	H(2) ¹⁴	3.60	H(1)	H(12) ¹⁰	2.40
H(1)	H(16) ¹⁰	2.87	H(1)	H(11) ¹⁰	2.88
H(2)	H(17) ²	2.82	H(2)	H(16) ¹⁰	2.87
H(2)	H(10) ¹	3.01	H(2)	H(19) ¹⁰	3.26
H(2)	H(19) ²	3.29	H(2)	H(18) ²	3.32
H(3)	H(11) ⁵	2.53	H(3)	H(16) ¹¹	3.08
H(3)	H(9) ⁵	3.28	H(3)	H(14) ¹¹	3.30
H(3)	H(10) ⁵	3.47	H(3)	H(17) ¹¹	3.58
H(4)	H(14) ¹¹	2.87	H(4)	H(12) ¹¹	3.12
H(5)	H(11) ¹⁰	3.06	H(5)	H(12) ¹⁰	3.08
H(5)	H(13) ⁸	3.23	H(6)	H(14) ⁷	2.61
H(6)	H(15) ⁷	3.40	H(7)	H(15) ⁸	2.62

Table S-22. Non-bonded Contacts out to 3.60 Å (continued)

atom	atom	distance	atom	atom	distance
H(7)	H(13) ⁸⁾	3.59	H(8)	H(8) ⁸⁾	2.44
H(8)	H(15) ⁸⁾	2.72	H(8)	H(13) ⁸⁾	3.34
H(9)	H(12) ¹¹⁾	2.43	H(9)	H(13) ¹¹⁾	2.76
H(9)	H(14) ¹¹⁾	2.96	H(10)	H(17) ⁷⁾	2.71
H(10)	H(19) ⁵⁾	2.81	H(11)	H(13) ¹¹⁾	2.73
H(11)	H(12) ¹¹⁾	3.60	H(12)	H(13) ¹¹⁾	3.43
H(13)	H(13) ¹¹⁾	3.05	H(16)	H(19) ¹³⁾	2.79
H(17)	H(19) ¹³⁾	2.74	H(19)	H(19) ¹³⁾	3.07

Symmetry operations

(1)	-X+1,-Y+1,-Z	(2)	-X+1,Y+1,-Z+1/2
(3)	X,Y+1,Z	(4)	X,-Y+1,Z-1/2
(5)	-X+3/2,Y+1/2,-Z+1/2	(6)	-X+3/2,Y-1/2,-Z+1/2
(7)	X,-Y,Z-1/2	(8)	-X+1,Y,-Z+1/2
(9)	X+1/2,-Y+1/2,Z+1/2	(10)	X-1/2,-Y+1/2,Z-1/2
(11)	-X+3/2,-Y+1/2,-Z+1	(12)	X,-Y,Z+1/2
(13)	-X+3/2,-Y-1/2,-Z+1	(14)	-X+1,Y-1,-Z+1/2